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FEASIBILITY STUDY OF HIGH-TEMPERATURE SYNTHETIC-AIR HEATER FOR USE WITH A MACH 8 TO 9 HYPERSONIC TUNNEL

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and Harold G. Price, Jr.

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SUMMARY

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Calculations and preliminary experiments have demonstrated the feasibility of a synthetic-air heater that could be used to supply heated air to a Mach 8.5 hypersonic test facility with true flight temperature and pressure simulation. The heater concept involves mixing strongly heated nitrogen and preheated nitric oxide and utilizing the exothermic decomposition of the nitric oxide to increase the mixture temperature.

Calculations of the heat released because of the reaction of nitric oxide in a pebble-bed preheater and preliminary experiments of its decomposition in a packed bed have shown that the nitric oxide can be heated to 1300° K without excessive decomposition. Calculations of the high-temperature decomposition of nitric oxide - nitrogen mixtures have shown that the reaction time is about 0.4 millisecond and probably will be controlled by mixing considerations. Nitrogen was heated to temperatures approaching 3000° K in a small graphite pebble bed without any significant formation of cyanogen. Recommendations for future work include the investigation of design and operational changes to extend the operational life of the graphite susceptor and experimental studies of the mixing and reaction of hot nitric oxide and nitrogen.

INTRODUCTION

A major obstacle to the development of hypersonic air-breathing engines has been the lack of suitable ground test facilities. At the present time, existing blowdown facilities that are large enough to accommodate full-scale engines can produce clean air at stagnation temperatures and pressures high enough to simulate Mach 5 or 6 test conditions for periods of a few minutes. Improvements in refractory materials may allow some gains in temperature over the currently available alumina pebble beds. Although electric-arc heaters are capable of heating air to much higher temperatures than those possible with ceramic-storage heaters, the use of the former for a large facility would

TABLE I. - CALCULATED EQUILIBRIUM TEMPERATURE

FOR MIXTURES OF 41.996 PERCENT NITRIC OXIDE -

58.004 PERCENT NITROGEN BY VOLUME

[Nitrogen temperature, 3000° K.]

Chamber pressure, atm	Nitric oxide temperature, °K				
	1100	1300	1500	1700	1900
	Calculated equilibrium temperature, °K				
34.02	----	3107	3164	3220	3276
68.05	3064	3124	3184	3244	3302
102.1	3071	3132	3194	3255	3315
136.1	3075	3137	3200	----	----
170.1	3078	3141	3204	----	----
204.1	3080	3144	3207	----	----

require very large quantities of electric power. Operation of electric-arc heaters at the required high pressure levels (100 to 200 atmospheres) has not yet been demonstrated.

At Mach numbers greater than about 9, dissociation of the air at stagnation conditions produces significant quantities of atoms that are chemically frozen during the tunnel nozzle expansion, so that facilities which expand air from stagnation conditions do not simulate free-flight conditions. At Mach numbers above 9, flight testing may be necessary to resolve the shortcomings of ground facilities. An immediate region of interest, therefore, for true simulation in a large facility is in the Mach number range between 6 and 9.

A method for producing high-temperature, high-pressure air to simulate the above Mach number range has been suggested (R.S. Brokaw and F.E. Belles of Lewis) that utilizes the exothermic decomposition of nitric oxide. The basic proposal is to simulate the composition of air by using a mixture of nitrogen and nitric oxide in the correct proportions (43.7 percent NO and 56.3 percent N_2 by weight). Nitrogen is preheated to a temperature (~3000° K), which is limited by the loss of bed material or cyanogen formation in a graphite pebble bed. (Heating of nitrogen in a small graphite resistance heater to temperatures of about 2775° K has already been demonstrated in ref. 1.) Nitric oxide would be preheated to a temperature (~1300° K) limited by the onset of the dissociation reaction

$$2NO \rightarrow N_2 + O_2 \qquad \Delta H_f = 21.6 \text{ kcal/mole} \qquad (I)$$
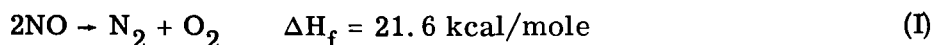
(Symbols are defined in appendix A.) The two preheated gases would then be mixed in a reaction chamber and expanded through a tunnel nozzle. Decomposition of the nitric oxide at the mixture temperature will be shown to rapidly approach equilibrium conditions. Equilibrium temperatures for the mixture have been calculated by using the IBM 7094 computer program of reference 2. The results are given in table I.

Although other decomposition reactions such as nitrous oxide have been investigated (refs. 3 to 5), the present proposal offers some clear advantages over the use of decomposed nitrous oxide for tunnel testing. First, nitric oxide has a higher decomposition temperature than that of nitrous oxide, which allows more preheat. Secondly, the mixing of nitric oxide with strongly heated nitrogen allows the decomposition reaction to proceed at a high rate so that heat-transfer losses to the containing vessel can be minimized. The decomposition of nitrous oxide at lower temperatures (ref. 6), has indicated that secondary reactions which result in the formation of nitrogen dioxide degrade the final reaction temperature. At much higher temperatures, species such as nitrogen dioxide would not be thermodynamically stable, and the decomposition to nitrogen and oxygen should predominate.

The purpose of this investigation is to perform preliminary calculations and experimental investigations to establish the feasibility of the proposed synthetic-air heater. Chemical kinetic and heat-transfer calculations are given for a pebble bed that was sized to heat 17.60 pounds per second of nitric oxide to 1300° K for a 2-minute run. The total synthetic-air flow of 40 pounds per second could supply a Mach 8.5 facility with a 4-foot-diameter test section. Experiments are described that involved the heating of nitric oxide in an alumina-packed heater at pressures up to 120 pounds per square inch absolute and temperatures up to 1500° K and the heating of nitrogen in a graphite pebble bed at a pressure of 1000 pounds per square inch absolute and temperatures up to 3000° K.

DECOMPOSITION OF NITRIC OXIDE

Reaction Mechanism and Rate Constants

The decomposition of nitric oxide has been the subject of a number of experimental investigations. The low-temperature decomposition has been studied in alumina-packed flow reactors in the range 973° to 2073° K (ref. 7) and in quartz vessels at temperatures of 1170° to 1530° K (ref. 8). The high-temperature reactions have been studied in shock tubes to temperatures of 4300° K (refs. 9 and 10). The low-temperature studies established that the decomposition proceeded by a combination of a zero-order, surface-catalyzed reaction and the bimolecular reaction (I), between the temperatures of 1373° to 1673° K. The reactions, however, were carried out at very low partial pressures of nitric oxide, which favored the surface reaction. The measured rate in the shock tube investigations was found to be the sum of the direct dissociation reaction

$$NO + Ar \rightarrow N + O + Ar \qquad (II)$$

and the bimolecular reaction (I). Results of these investigations are summarized in figure 1, where the log of the rate constant is plotted against reciprocal temperature. The
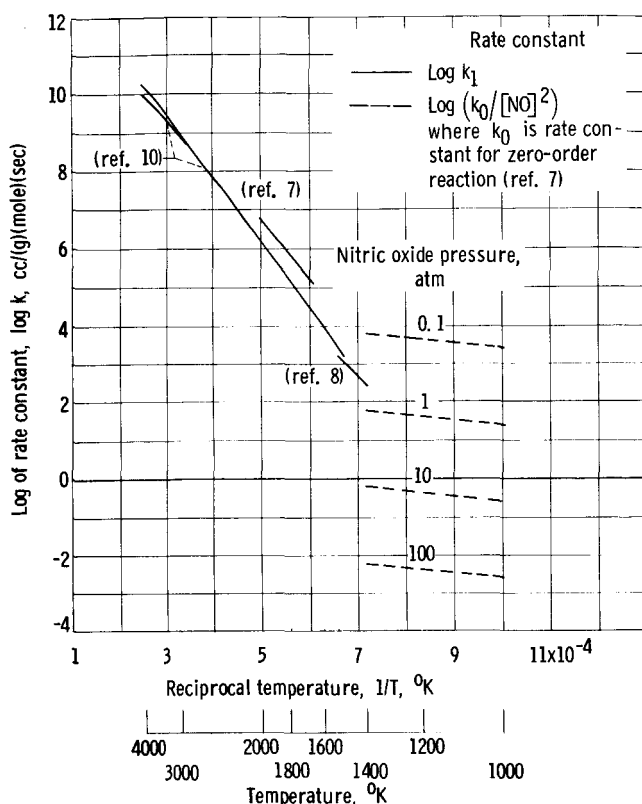
Figure 1. - Comparison of reaction rate constants for decomposition of nitric oxide.

rate constant for the zero-order reaction (ref. 7) is plotted as $k_o/[NO]^2$ to compare it with the bimolecular rates. For the ranges of temperatures and pressures of interest in the present investigation, the zero-order reaction is probably unimportant. For example, the extrapolation of the line for reference 10 in figure 1 down to $1300°$ K results in a rate constant for the bimolecular reaction that is almost four orders of magnitude higher than the surface reaction at 100 atmospheres; however, there remains a region of some uncertainty in extrapolating the results of the bimolecular rate constant down to temperatures of $1100°$ to $1300°$ K.

Nitric Oxide Heater Calculations

Although there is some uncertainty in the existing rate constants for the nitric oxide decomposition reaction, it was desirable at this time to calculate the amount that would be dissociated at the appropriate test conditions. The conditions chosen were a stagnation pressure of 100 atmospheres and an initial bed temperature of $1300°$ K.

An alumina pebble bed was sized for a flow rate of 17.60 pounds per second of nitric oxide by using an existing computer program. This nitric oxide flow rate with the correct proportion of nitrogen would yield 40 pounds per second of high-temperature air. Because the computer program was not designed to include the effects of chemical reactions within the bed, an approximate iterative hand calculation was made by using the computer calculations as initial conditions. The following assumptions were made in addition to those already made in the heat-transfer program:

(1) The bimolecular reaction (I), using the rate constant of reference 10, was used:

$$k_1 = 4.8 \times 10^{23} T^{-2.5} \exp[-85\ 500/RT] \qquad cc/(mole)(sec) \qquad (1)$$

(2) No secondary reactions were considered.

(3) Since the heat capacity of the bed material was about 170 times that of the gas, the bed was considered a heat sink, and its temperature rise due to the reaction neglected.
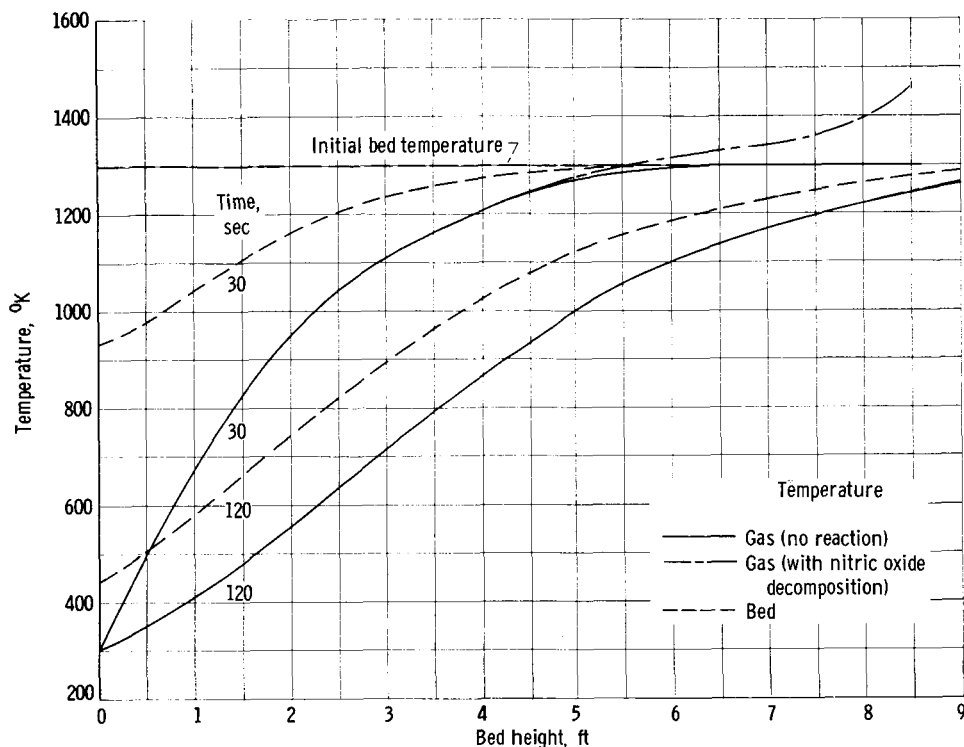
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Figure 2. - Calculated temperature history for nitric oxide pebble bed; bed diameter, 2.5 feet; ball diameter, 0.5 inch; pressure, 100 atmospheres; mass flow rate, 17.60 pounds per second.

(4) The gas film heat-transfer coefficient was assumed to be controlling and constant throughout the bed.

The derivations of the equations that include heat-generation and heat-transfer terms are given in appendix B. The bed was divided into 0.5-foot-high increments, and an approximate iterative solution obtained.

The results of the calculation are shown in figure 2 for times of 30 and 120 seconds from the start of the run. At 30 seconds and the top of the bed, 11.9 percent of the NO had been converted. Approximately 46 percent of the heat of reaction associated with this conversion is lost to the bed. In this case it would be advantageous to operate the bed 40° to 50° K lower in initial temperature because the loss in sensible enthalpy is much less than the loss in the reaction enthalpy at the higher temperature. At 120 seconds, the bed temperature has dropped to temperatures where the extent of reaction is negligible. It appears possible to design a bed so that the initial temperature profile and gas residence time would minimize the dissociation reaction.

Calculations of High-Temperature Reaction

At temperatures corresponding to the mixture temperature for 42 percent nitric oxide and 58 percent nitrogen by volume and for the reactions going to equilibrium, other reactions in the nitrogen-oxygen system must be considered.
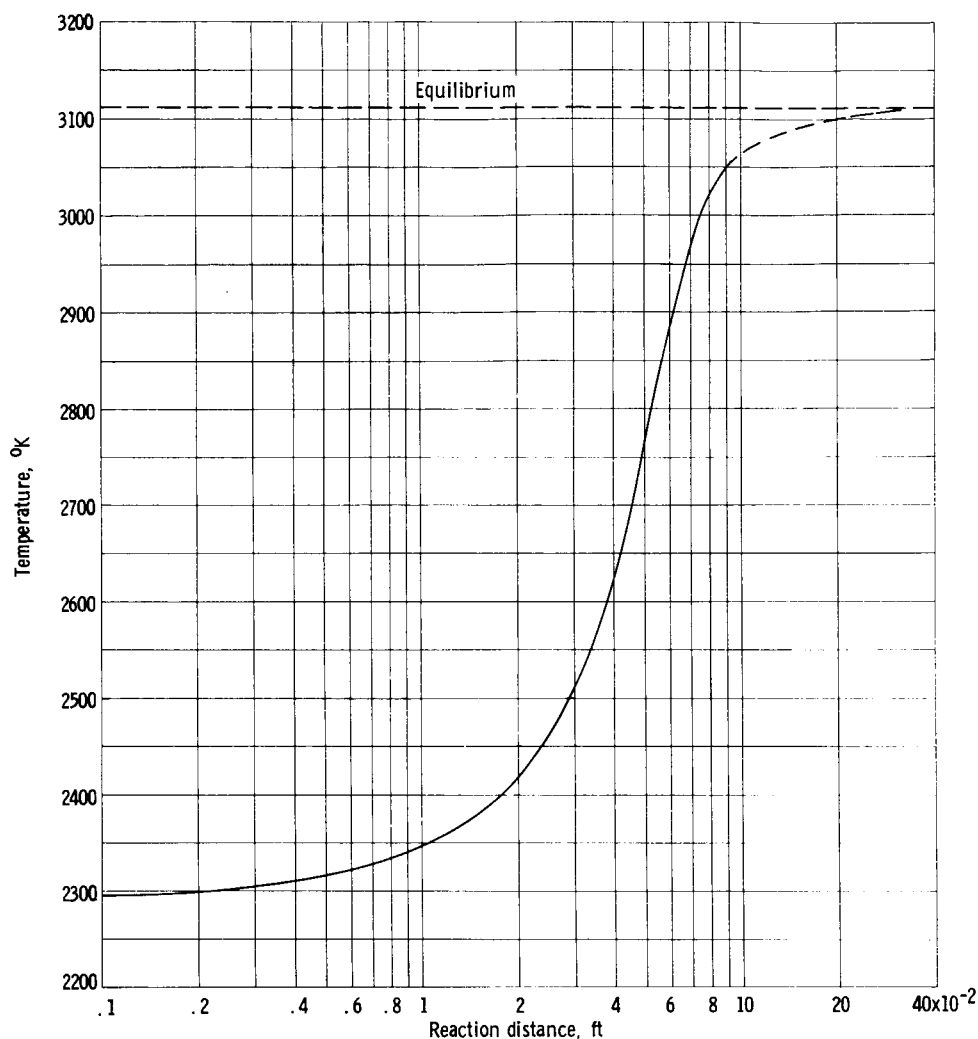
Figure 3. - Reaction progress for nitric oxide - nitrogen mixture; mole fraction of nitric oxide, 0.41996 (1300° K); mole fraction of nitrogen, 0.58004 (3000° K).

A calculation of the reaction of the hot nitric oxide - nitrogen mixture was performed by using the chemical kinetic computer program of reference 11. A mixture temperature of 2291° K was computed and used as the starting temperature for a constant area reaction process. The initial mixture velocity was assumed to be 400 feet per second. The reactions and rate constants used in the calculation are given in table II. Results of calculations for a chamber pressure of 500 pounds per square inch absolute are given in figures 3 and 4. The calculations were not carried to near equilibrium composition because of excessive computer time. The curves of figures 3 and 4 were extrapolated to near equilibrium conditions by a linearization of the rate equations. The extrapolation is valid because a plot of $\log(X_{NO} - X_{NO, Eq})$ against time is linear toward the end of the kinetic calculations. The reaction time for 99.9 percent conversion is 0.4 millisecond; thus the time required to mix the hot nitrogen and nitric oxide will probably control the process.
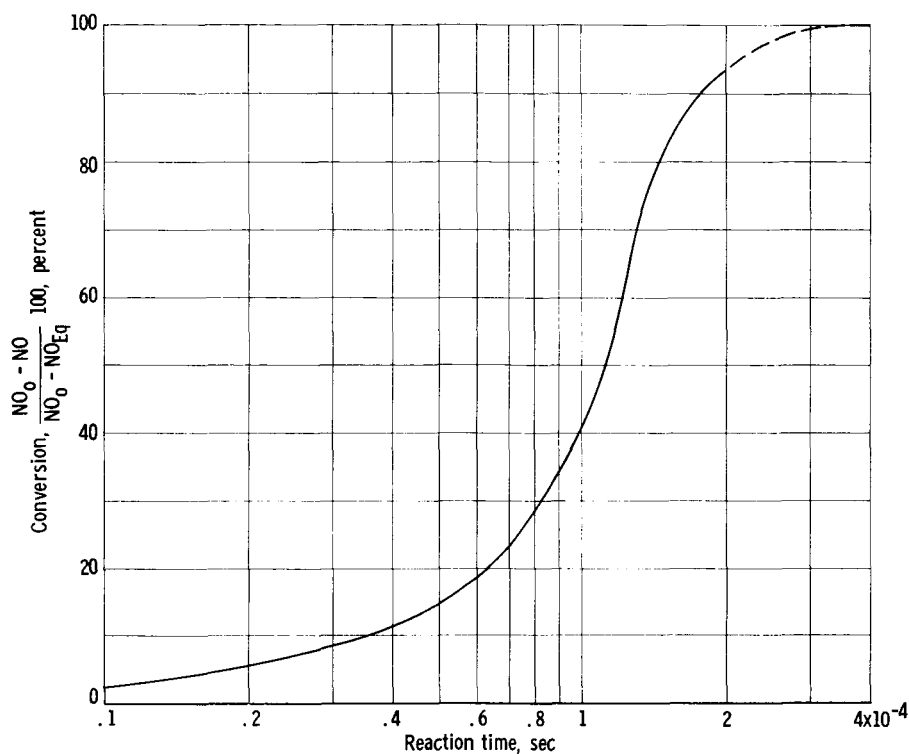
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Figure 4. - Reaction history for nitric oxide - nitrogen mixture.

TABLE II. - REACTIONS AND RATE CONSTANTS

$\left[\text{Forward rate constant, } k_f = BT^n \exp{-E/RT}, \text{ where } T \text{ is}\right.$
$\left.\text{temperature and } R \text{ is gas constant.}\right]$

Reaction	Preexponential factor, B, $(cm^3)(moles)(sec)$	Temperature exponent, n	Activation energy, E, cal/mole	Reference
(I) $N_2 + O_2 \rightleftharpoons 2NO$	9.1×10^{24}	-2.5	128 500	[a]14
(II) $NO + M \rightleftharpoons N + O + M$	5.18×10^{21}	-1.5	150 000	14
(III) $O_2 + M \rightleftharpoons O + O + M$	1.137×10^{25}	-2.5	118 000	
(IV) $N_2 + M \rightleftharpoons N + N + M$	2.97×10^{21}	-1.5	225 000	
(V) $O + NO \rightleftharpoons O_2 + N$	3.2×10^{9}	1.0	39 000	
(VI) $O_2 + NO \rightleftharpoons O + NO_2$	7.8×10^{11}	0	45 000	
(VII) $O + NO + M \rightleftharpoons NO_2 + M$	3.12×10^{17}	-.5	0	
(VIII) $NO + NO \rightleftharpoons NO_2 + N$	2.7×10^{14}	-1.0	77 300	
(IX) $NO + N_2 \rightleftharpoons N_2O + N$	2.7×10^{14}	-1.0	110 600	
(X) $N_2O + M \rightleftharpoons N_2 + O + M$	2.07×10^{22}	-2.0	62 000	

[a]Forward rate constant k_f was calculated from reverse rate constant k_r of
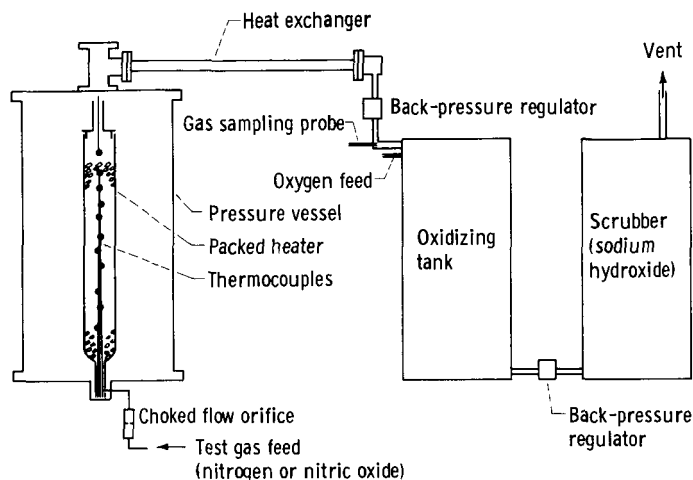ref. 10.

Figure 5. - Experimental apparatus for nitric oxide decomposition tests.

EXPERIMENTAL

Nitric Oxide Decomposition Tests

Experimental measurements of the extent of the low-temperature decomposition reaction (I) were made in an alumina flow reactor at pressures of 4 atmospheres and higher.

Apparatus. - The experimental apparatus (fig. 5) consists of a packed heater through which nitric oxide is passed, a heat exchanger to cool the gases, and an exhaust system to safely dispose of the toxic nitric oxide.

The heater consists of a 2-inch-inside-diameter alumina cylinder with a 3-foot-high section heated by externally wound tungsten resistance wire. The cylinder is filled with 1/8-inch-diameter high-purity alumina balls. The assembly with external insulation is contained in a pressure vessel. The heater is instrumented with platinum - platinum-13-percent-rhodium thermocouples located axially along the cylinder and at the gas exit. Gas flow into the heater is controlled by means of choked-flow orifices. Pressure in the heater section is maintained by a back-pressure regulator located at the exit of the heat exchanger.

The exhaust system consists of an oxidizing tank where oxygen is added to the nitric oxide to form nitrogen dioxide followed by a scrubber, which is filled with a caustic solution. Neutralization of the acids occurs in the caustic solution.

Operating procedure. - The heater section is evacuated to remove all oxygen and water and filled with nitrogen at a positive pressure. The bed is brought up to temperature, and the system pressurized for a run. Nitrogen is passed through the bed with the electrical power on until gas and bed attain a steady-state temperature. The gas flow is then switched to an equivalent flow of nitric oxide. Small amounts of decomposition will be detectable by the exit gas thermocouple and larger amounts by the change in the bed temperature profile with time. Gas samples can be removed at the water-cooled section and analyzed for decomposition products, predominantly nitrogen dioxide formed by reactions (I) and (VI) (table II).

Preliminary results. - Initial runs with nitric oxide at a pressure of 4 atmospheres and a temperature of 1422° K resulted in dissociation of about 1 percent, based on calculations from the temperature rise of the exhaust gas from the heater. At the equivalent test conditions, calculations of the amount of dissociation were made by using the rate equations of references 7 and 10. These rates resulted in values of 7.33 and 0.86 per-

Figure 6. - Pilot graphite pebble bed.

cent dissociation, respectively. The experimental result compared most favorably with the rate expression of equation (I) (ref. 10).

Nitrogen Heating Tests

Apparatus. - The pebble-bed heater (fig. 6) consists of a pressure vessel designed for 1200 pounds per square inch absolute and containing a graphite susceptor filled with graphite balls, 0.25 inch in diameter. The susceptor is 5 feet long with an 8.5-inch inside diameter and a 1-inch-thick wall. It is wrapped with graphite-felt insulation and is heated inductively with a power supply of 3000 cycles per second. The induction coil is water cooled.

Instrumentation used during the tests included radiation pyrometers sighted on the susceptor wall and on a graphite well submerged below the upper ball layers of the bed. The well was considered to be a blackbody. Tungsten - tungsten-26-percent-rhenium thermocouples were located along the outside susceptor wall. Measurements of the exit gas from the bed were made with a tungsten - tungsten-26-percent-rhenium thermocouple and gas sampling probes.

Operating procedure. - Before a nitrogen heating test, the bed was evacuated and filled with helium three times to eliminate oxygen from the bed. The bed was then heated induc-
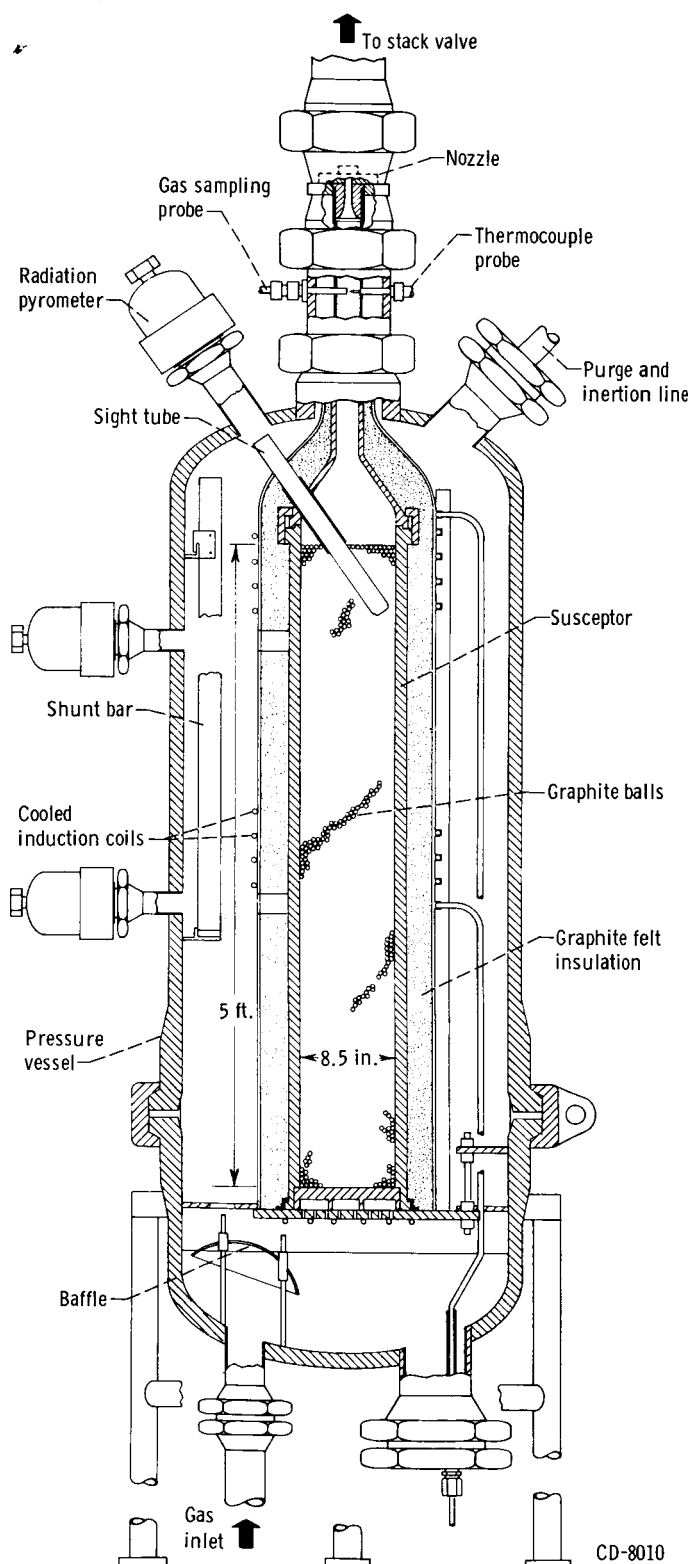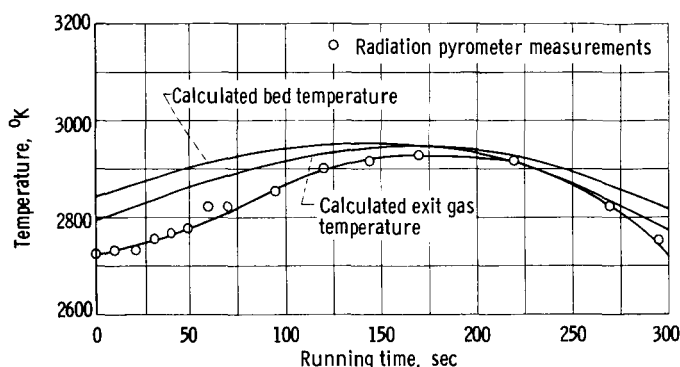
Figure 7. - Temperature-time history of nitrogen heating test; mass flow rate, 0.2 pounds per second.

tively in a helium atmosphere at slightly above atmospheric pressure for about $1\frac{1}{2}$ hours. When the desired bed temperature was reached, as indicated by a radiation pyrometer sighting on the susceptor, the heating cycle was changed to intermittent operation to maintain the bed at temperature. The bed was soaked from 2 to 4 hours to arrive at a more uniform radial temperature profile. Before the blowdown cycle, electrical power was shut off, the stack valve was opened, and pressurization with nitrogen was started. Flow rate was controlled by a choked nozzle at the exit of the instrumentation section and by maintaining the inlet pressure at the desired level. During the run, at preprogramed times of 45 to 140 seconds, gas samples were removed through a sonic orifice water-cooled probe. The samples were collected in pre-evacuated bottles for periods of 15 seconds. Exhaust gas temperature, susceptor, and bed-top temperatures were continuously recorded. At the completion of the run, the nitrogen supply valve was closed, and the bed was allowed to bleed down to atmospheric pressure. A pressure of 2 to 5 pounds per square inch gage of helium was maintained in the bed during final cooldown to prevent contamination by oxygen. The collected gas samples were later analyzed on a mass spectrometer for cyanogen and other trace gases.

Results. - A series of six tests was run, which covered a range of initial bed temperatures of 2200° to 3000° K with nitrogen flow rates of 0.15 and 0.35 pounds per second and a pressure of 1000 pounds per square inch absolute. Figure 7 shows a temperature-time history of the bed at the top radiation pyrometer location for the highest temperature run. Time is taken as zero at the point where initial pressurization with the test gas is complete. Heat-transfer calculations were performed by using the heat-transfer data given in reference 12. The calculations were programed for an iterative solution of the nonsteady heat-transfer equations in packed beds for the IBM 7094 computer. The initial axial bed temperature profile and calculated mass flow through the bed were used as input to the program. The bed mass flow was corrected for cold gas leakage, through joints in the graphite susceptor, which bypassed the bed and mixed with the hot gas. The amount of leakage was determined from a separate investigation.

With this correction, the calculated bed temperature history (fig. 7) agrees reasonably well with the measured temperatures. The rise in bed temperature at the beginning of the run is caused by the initial axial temperature profile of the bed, which was hotter toward the middle. The measured gas temperature, as indicated by the thermocouple probe, was also brought into satisfactory agreement when dilution with the cooler leak-
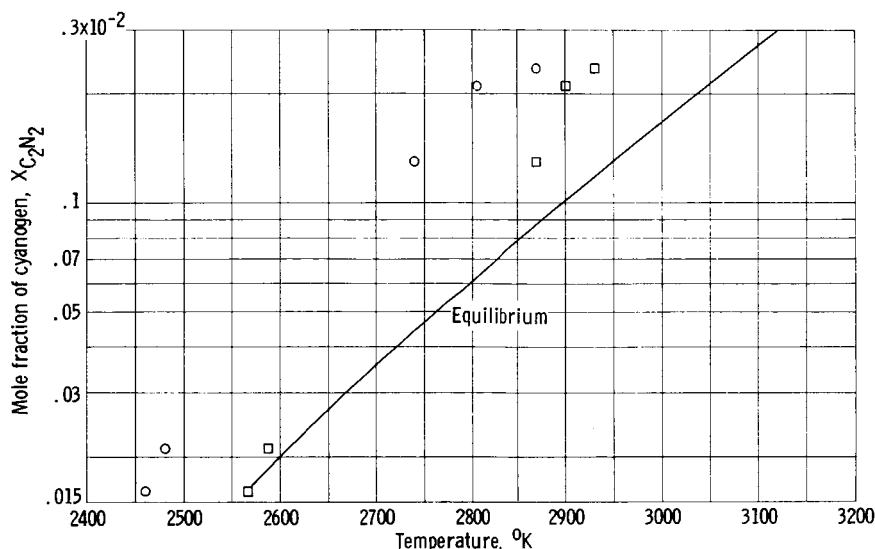
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Figure 8. – Comparison of cyanogen from gas samples to equilibrium calculations.

age gas was considered.

Gas samples taken at various times during the run were analyzed for cyanogen with a mass spectrometer. The measured mole fraction of cyanogen is plotted against the bed temperature in figure 8. The solid curve has been calculated for equilibrium. Equilibrium mole fraction of CN is included in the total as C_2N_2. The circles are plotted at the temperature indicated by the top radiation pyrometer, and the squares at the calculated exit gas temperature are taken from figure 7. The differences between the experimental points and equilibrium curve are insignificant in view of the uncertainties in the dissociation energy of cyanogen. The amount of cyanogen formed does not appear to offer any problems with respect to enthalpy loss or to toxicity.

After six runs, the graphite balls lost 0.25 percent of their original weight. Carbon deposits were found on the nozzle and on the probes after each run. When the bed was disassembled, the graphite susceptor was observed to have lost as much as 3/16 inch from its thickness near the center of the heated region. Since the susceptor temperature was highest near the center, any vaporization of graphite would be expected to make the situation progressively worse because the thinner section has a higher electrical resistivity.

RECOMMENDATIONS FOR FUTURE WORK

Preliminary calculations and tests in which nitrogen and nitric oxide were heated in packed beds have demonstrated the feasibility of a synthetic-air heater for supplying a hypersonic tunnel. Some of the more difficult developmental problems remain, such as the mixing, reaction, and containment of the high-temperature, high-pressure gas.

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These problems should be investigated on a small scale before embarking on the design and construction of a large facility.

The loss of graphite by vaporization from the susceptor was probably aggravated by the long heat soak at temperatures of 3000° K or above. Graphite vapor is probably removed from the surface of the hot susceptor by convective currents set up in the helium during the heating and soaking periods and redeposited on cooler parts of the graphite felt insulation. The long heat soak was used to insure a uniform radial temperature profile in the bed because initial calculations with an assumed effective bed thermal conductivity indicated that such a soak period might be necessary. This remains conjecture, however, because the high-temperature levels prevented the measurement of a radial temperature profile. Lacking such data, the need for the long soak period has not been established. A radial temperature profile could be measured at a lower temperature level to arrive at an effective thermal conductivity. Design changes that could increase the operational life of the susceptor are segmentation and separate control of the input power to eliminate hot regions and the use of a surface-pyrolyzed or graphite-tape-wrapped susceptor to introduce an insulating barrier to the diffusion process.

Problems of transportation and storage of nitric oxide at high pressure were made known recently by the work reported in reference 13, which investigated the decomposition of nitric oxide at low temperatures and pressures up to 400 atmospheres. The overall stoichiometry is given by

$$3NO \rightarrow N_2O + NO_2 \tag{XI}$$

Substantial amounts of decomposition were found to occur at a pressure of 200 atmospheres and room temperature, over a period of several days. In addition to the enthalpy loss due to reaction (XI), there could be hazards because of the formation of highly reactive nitrogen dioxide. A possible solution to the storage problem would be to transport the nitric oxide at low pressures or as a liquid at its boiling point. The nitric oxide could be stored on site as a liquid in a vacuum-jacketed tank and pressurized only when used.

Operating costs for a large facility will depend on the availability and ultimate cost of nitric oxide in tonnage quantities. At present there is little commercial use for nitric oxide so that its cost is high; however, nitric oxide is an intermediate in the production of nitric acid by oxidation of ammonia and could be separated from the process at low potential cost if there were sufficient demand.

SUMMARY OF RESULTS

Calculations and preliminary experiments have demonstrated the feasibility of a

synthetic-air heater that could be used to supply true-temperature air to a Mach 8.5 hypersonic test facility. Calculations of the heat released because of the reaction of nitric oxide in a pebble-bed preheater and preliminary experiments of its decomposition have shown that the nitric oxide can be heated to at least 1300° K. Calculations of the high-temperature decomposition of nitric oxide - nitrogen mixtures have shown that the reaction time is short (0.4 msec under the chosen conditions).

Nitrogen was heated to temperatures approaching 3000° K in a small graphite pebble bed without any significant formation of cyanogen. Loss of graphite from the susceptor was excessive, but it appears to be a problem that can be solved by eliminating long periods of heat soaking at high temperatures and by more uniform heating of the susceptor.

Recommendations for future work include the investigation of design and operational changes to extend the operational life of the graphite susceptor and experimental studies of the mixing and reaction of hot nitric oxide and nitrogen. The production, transportation, and storage of large quantities of nitric oxide that would be used at high pressures requires engineering study.

Lewis Research Center,
    National Aeronautics and Space Administration,
   Cleveland, Ohio, April 9, 1965.

APPENDIX A

SYMBOLS

A	bed cross-sectional area	$\bar{v}$	mean gas velocity
A_f	bed cross-sectional void area	$\dot{w}$	mass flow rate
C_p	gas heat capacity	X	mole fraction of nitric oxide reacted
G	mass velocity per unit area		
ΔH_f	heat of reaction	ξ	dimensionless bed length
h_g	heat-transfer coefficient	ρ	gas density
k	reaction rate constant	[ ]	concentration
$\Delta \ell$	incremental bed length	Subscripts:	
$\mathcal{M}$	molecular weight	c	chamber
P	pressure	Eq	equilibrium
Q_{chem}	heat released per incremental bed length	g	gas
		k, n	iteration steps
R	gas constant	o	initial conditions
S	surface area per unit volume	ref	gas reference condition, no reaction
T	temperature		
t	time	t	final time

APPENDIX B

CALCULATION OF NITRIC OXIDE DECOMPOSITION AND

HEAT TRANSFER IN STORAGE HEATER

The rate for the bimolecular decomposition of nitric oxide

$$2NO \rightleftharpoons N_2 + O_2$$
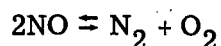
is given by the rate equation

$$\frac{d[NO]}{dt} = 2k_1[NO]^2 \tag{B1}$$

Equation (B1) can be integrated to give

$$\frac{1}{[NO]_t} - \frac{1}{[NO]_o} = 2k_1 \Delta t \tag{B2}$$

For small fractions of converted nitric oxide, equation (B2) can be written as

$$\frac{X}{1 - X} = \frac{P}{RT} (2k_1 \Delta t) \tag{B3}$$

where X is the mole fraction of decomposed nitric oxide and P is the total pressure. The rate constant k_1 is taken from reference 10 as

$$k_1 = 4.8 \times 10^{23} \ T^{-2.5} \exp[-85\ 500/RT] \qquad cc/(mole)(sec) \tag{B4}$$

The incremental time Δt is given by $\Delta t = \Delta \ell / \overline{v}$, where $\Delta \ell$ is the incremental bed height, $\overline{v}$ is the mean gas velocity $\dot{w}/\rho A_f$, and A_f is the cross-sectional void area of the bed.

The heat released per incremental bed length is

$$Q_{chem} = \frac{\dot{w}}{\mathscr{M}} \ X \ \Delta H_f \tag{B5}$$

where ΔH_f is the heat of formation per mole and $\mathscr{M}$ is the molecular weight.

When a heat balance for the incremental bed height $\Delta \ell$ is set up by using the calcu-

lated heat-transfer and gas temperature profiles without reaction as a reference condition, the increase in enthalpy of the gas at the kth step is given as

$$\frac{\dot{w}}{\mathcal{M}} C_p \left(T_g - T_{ref}\right)_k = \sum_{n=1}^{k} \left[\frac{\dot{w}}{\mathcal{M}} X_n \Delta H_f - h_g SA \Delta \ell \left(T_g - T_{ref}\right)_n\right] \tag{B6}$$

where h_g is the gas film heat-transfer coefficient, S is the surface area of the balls per unit bed volume, $A \Delta \ell$ is the incremental bed volume, and T_g and T_{ref} are the gas and reference gas temperatures, respectively.

The temperature increase due to reaction is then

$$\left(T_g - T_{ref}\right)_k = \sum_{n=1}^{k} \left[\frac{X_n \Delta H_f}{C_p} - \frac{h_g S \Delta \ell}{C_p \, G/\mathcal{M}} \left(T_g - T_{ref}\right)_n\right] \tag{B7}$$

The heat-transfer term has been rewritten in terms of the mass velocity per unit area G and has the form of a dimensionless length parameter ξ (ref. 12) times the temperature difference between the gas and reference gas temperatures. Since the rate constant, and hence X, is a function of the local gas temperature, equation (B7) must be solved by an iterative process to determine a new gas temperature profile.

A simplifying assumption used in the solution was that the bed temperature would remain equal to the reference condition because its heat capacity per unit bed volume is very large compared with that of the gas. The consequences of the assumptions are that the chemical heat-generation terms have no effect on heat transfer from the bed to the gas.

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